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LCA OF CHEMICALS

Life cycle assessment of alternatives for waste-solvent valorization: batch and continuous distillation vs incineration

Patricia Luis · Antonio Amelio · Steven Vreysen · Vicenza Calabro · Bart Van der Bruggen

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Abstract
Purpose The goal and scope of this research is focused on the application of life cycle assessment (LCA) to evaluate two alternatives (batch and continuous distillation and incineration with energy recovery) for the treatment of four waste-solvent mixtures typically produced in the chemical industry: acetonitrile–toluene, acetonitrile–toluene–tetrahydrofuran (THF), ethyl acetate–water and methanol–THF, with several compositions in order to determine the most appropriate technology depending on the characteristics of the mixture.
Materials and methods Ecosolvent® v.1.0.1 software is used to perform the LCA, considering two scenarios and the following methods of impact assessment: Eco-indicator 99, cumulative energy demand, method of ecological scarcity (UBP'97), global warming potential and CO_2 balances.
Results and discussion Results show that distillation gives more environmental credits for the recovery of the most concentrated compound in acetonitrile–toluene mixtures. However, when THF is present in the waste solvent even in small quantities, it has to be recovered due to the high impact associated to its manufacture. Regarding the mixture ethyl acetate–water, distillation takes advantage at concentrations of ethyl acetate higher than 50 wt%, and for the mixture methanol–THF, recovery of methanol is not advantageous from an environmental point of view, but the recovery of THF is clearly necessary to decrease the total impact.
Conclusions From this study, it can be concluded that those compounds that yield a great environmental burden during the production step should be always recovered in order to minimize the total impact, even if they represent the minor concentration in the mixture. In case that similar impact is produced during the solvent production, the major compound in the mixture should be the target for recovery.

Keywords Distillation · Ecosolvent · Incineration · Life cycle assessment · Solvent recovery

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P. Luis (✉) · B. Van der Bruggen
Department of Chemical Engineering, Process Engineering for Sustainable Systems (ProcESS), KU Leuven, W. de Croylaan 46, 3001 Leuven, Belgium
e-mail: patricia.luis@cit.kuleuven.be

A. Amelio · V. Calabro
Department of Modeling for Engineering, University of Calabria, Arcavacata Campus, via P. Bucci, Arcavacata di Rende, 87036 Cosenza, Italy

S. Vreysen
KH Kempen University College, Kleinhoefstraat 4, 2440 Geel, Belgium

1 Introduction

Large quantities of organic solvents are used by the chemical industry and related industries. Most of them have hazardous properties such as toxicity and high volatility, which involves special consideration in the design of chemical products and processes and in the management of waste solvent (Jimenez-Gonzalez et al. 2005; Alfonsi et al. 2008). An optimal waste-solvent management aims at minimizing hazardous waste, reducing raw material input and lowering emission of toxic substances to the environment (Seyler et al. 2006). In addition, waste-solvent treatment is not only important from an environmental of human health point of view but also with respect to an optimal use of natural resources since material or energy can be recovered/reused (Seyler et al. 2004). Different treatment methods can be considered. Solvent recovery by distillation or solvent incineration are common technologies used on an industrial scale (Jankowitsch et al. 2001; Romero-Hernandez 2004;

Seyler et al. 2006). The decision making over which technology is the most appropriate is not straightforward (Beaver et al. 2002; Benko et al. 2006), mainly due to the kind of waste solvent (toxicity, cost, legislation, thermodynamic properties, etc.) and to the different advantages/disadvantages of each technology (e.g., reduction of light fuel oil by the use of waste solvents as fuels for steam and electricity production in the incineration and saving of solvents from the petrochemical solvent production by waste solvent recovery). The use of sustainability indicators that take into account environmental impacts in order to gather information depending on the composition of the mixture to be treated is of utmost interest.

Life cycle assessment (LCA) is a well-known tool used in the industry to evaluate the overall impact on the environment of the whole life cycle of processes and products (Bretz and Frankhauser 1997; Azapagic 1999; Geisler et al. 2005; Russell et al. 2005; Van der Vorst et al. 2010). LCA is a systematic method that can be successfully used in waste-solvent treatment since it considers all impacts on humans and the environment during the entire life cycle of solvents (including impacts from raw material extraction, solvent production, use of energy and ancillaries, as well as waste-solvent treatment; Hofstetter et al. 2003; Capello et al. 2007). The fact that the evaluation is done from the point at which materials are gathered from the earth until these materials are returned to the earth (Huijbregts 1998; Lifset 2006; Raymond et al. 2010) allows studying the positive impact achieved when material resources are reduced due to solvent recovery or energy production. Choosing the right treatment option is of high importance from an environmental point of view since waste solvents can either be recycled to save fresh solvents or be thermally treated recovering the chemically bound energy. Thus, incineration as well as distillation becomes the focus of attention in the waste-solvent management strategy in order to save raw materials and/or energy. In this context, it has already been shown that LCA is an interesting tool to establish preferences with regard to treatment options for selected (hazardous) waste streams which will be of great value during the decision-making process (Tukker 1999a, b, 2000; Hofstetter et al. 2003; Seyler et al. 2005, 2006; Capello et al. 2005; Benko et al. 2006), and even in the development of a waste management policy (Fullana i Palmer et al. 2011).

The methodology used in LCA includes the definition of goals and scoping, inventory analysis, impact assessment and interpretation. The goal and scoping of this research is focused on two treatment alternatives (i.e. distillation and incineration with energy recovery), which will be evaluated and compared for the treatment of four waste solvent mixtures typically produced in the chemical industry: acetonitrile–toluene, acetonitrile–toluene–tetrahydrofuran (THF), ethyl acetate–water and methanol–THF. Different concentrations of each mixture are evaluated in order to determine the most appropriate technology depending on the characteristics of the mixture. Thus, the waste solvent is considered as material resource in distillation since the solvent can be reused, which may be critical when the manufacture of virgin solvent contribute significantly to the environmental burden (Raymond et al. 2010; Wernet et al. 2010) and energy resource for incineration where energy (heat and/or electricity) is produced. The inventory creation, analysis and impact assessment have been performed with Ecosolvent v.1.0.1, a LCA free-software developed by Capello et al. (2007; 2008) to evaluate the LCA of waste solvents in the chemical industry. This tool allows a better approximation of results to the reality thanks to waste-solvent specific inventory models for distillation and incineration based on data from the industry that help to calculate waste-solvent specific inventory flows (e.g. emission flows and ancillary uses) as a function of a few input parameters (e.g. waste-solvent composition and treatment technology) (Capello et al. 2007). Thus, potential human and ecological effects can be calculated, and both treatment technologies can be compared.

2 Materials and methods

2.1 Waste-solvent mixtures under study

The azeotropic mixtures acetonitrile–toluene, acetonitrile–toluene–THF, ethyl acetate–water and methanol–THF are the object of this study. They are waste streams in several pharmaceutical and chemical companies, and they are mostly treated by means of incineration due to their toxic character. All solvent mixtures form azeotropes. For the separation of these azeotropic mixtures, azeotropic or extractive distillation has to be used. A second distillation is needed to purify the desired product (top or bottom product). Therefore, we take in account two distillation steps and compare this with incineration. In the used model, the unpurified product is incinerated with energy recovery. For the binary mixtures, three concentrations, i.e. 25, 50 and 75 wt%, will be considered. For the ternary mixture, the following compositions are studied: 33.3 wt% of each compound and mixtures with a major compound (50 wt%) and two minor compounds (25 wt% each). The studies are done in different situations, considering the recovery of each compound, this is, establishing a target recovery of 99 wt% purity of one of the components in the mixture.

2.2 Ecosolvent

Ecosolvent® v.1.0.1 (Safety and Environmental Group, Zurich, Switzerland) was developed by Capello et al. (2007, 2008) as a generic life cycle inventory tool that

combines life cycle inventory models of distillation and thermal treatment in hazardous waste incinerators and cement kilns. In addition, a wastewater treatment model for the disposal of aqueous distillation residues is also included. The tool is publicly available for download and use at no cost (www.sust-chem.ethz.ch/tools/ecosolvent).

The solvent incineration model used in this work considers a large solvent incineration plant, where liquid wastes, including spent organic solvents, distillation residues, mother liquors, waste oils, and highly organic charged wastewaters, are disposed (Capello et al. 2007), and steam and electricity are co-products obtained in this incineration plant. The total environmental impact is the summation of the impacts (positive values) caused by the use of supplemental fuel oil (I_{oil}), ancillaries (I_{anc}), the emission of CO_2 (I_{co2}), other emissions (I_{em}) and the reduction of environmental burdens (negative values) from the energy co-products (I_{energy}). The solvent distillation model (Capello et al. 2005, 2007) can consider nine multipurpose batch distillation processes, eight distillation columns on an industrial scale and two simple batch distillation columns for preliminary purification. The total environmental impact is calculated as the sum of the impacts (positive values) produced by predistillation treatment steps (I_{pre}), the use of steam (I_{st}), electricity (I_{el}), nitrogen (I_{n2}), ancillaries (I_{anc}), outlet air (I_{air}) and residue (I_{res}), treatment of wastewater (I_{ww}) and the reduction of environmental burdens (negative values) due to solvent recovery (I_{solv}). Thus:

Waste-solvent incinerator:

$$I_{inc} = I_{oil} + I_{anc} + I_{co2} + I_{em} + I_{energy} \quad (1)$$

Distillation:

$$I_{dist} = \left(I_{pre}\right) + I_{st} + I_{el} + I_{n2} + I_{anc} + I_{air} + I_{res} + I_{ww} + I_{solv} \quad (2)$$

A detailed description of the mathematical approach can be found in Capello et al. (2008). In this work, batch and continuous distillation have been compared.

2.3 Environmental indicators

Ecosolvent includes different methods for the impact assessment (Capello et al. 2007), such the Eco-indicator 99 (Goedkoop and Spriensma 2000), cumulative energy demand (Jungbluth and Frischknecht 2004), method of ecological scarcity—also called eco-scarcity or eco-points method (from the German name of the unit used—"Umweltbelastungspunkte", UBP'97) (Hischier 2004), global warming potential (IPCC 2001) and CO_2 balances. In this work, all those environmental indicators were considered in order to have a clear view of the limitations of the technology under different perspectives. It is important to mention that the ReCiPe impact assessment method has been recently developed by Goedkoop et al. (2009), which is an improvement on Eco-indicator 99. Also, the method of ecological scarcity has been updated from UBP'97 to UBP 2006 (Frischknecht et al. 2009) and IPCC 2007 is an update of the method IPCC 2001 developed by the International Panel on Climate Change (IPCC 2007). Ecosolvent does not include these methods yet, but still, it is worth using this tool for the performance of LCA analysis since it includes the remarkable possibility of comparing distillation versus incineration, which allows the orientation of LCA to applications in Chemical Engineering.

The *Eco-indicator 99* aims to quantify all emissions and resource uses as damages (Goedkoop and Spriensma 2000) that focuses on three categories: damage to human health, to ecosystem quality and to resources. The results for these three categories can be combined into a single score using default weighting factors, and score is expressed as eco-indicator 99 points. There is no absolute value of the indicators; they have only a relative value: similar processes might be compared based on the Eco-indicator scores. The scale of Eco-indicators is chosen in such a way that the value of 1 pt is representative for one thousandth of the yearly environmental load of one average European inhabitant (Goedkoop and Spriensma 2000; Benko et al. 2006). However, the most critical and controversial step in LCA is the weighting step. Goedkoop and Spriensma (2000) defined three damage models for the three types of endpoints (i.e. Human Health, Ecosystem Quality and Resources). The damage function presents the relation between the impact and the damage to human health or to the ecosystem. The damages to Human Health are expressed as Disability Adjusted Life Years (DALY) and a fate- (linking an emission to a temporary change in concentration), exposure- (linking this temporary concentration to a dose), effect- (linking the dose to a number of health effects) and damage- (linking health effects to DALYs using the number of years lived disabled and years of life lost) analyses are performed. The damages to Ecosystem Quality are expressed as the percentage of species that have disappeared in a certain area due to the environmental load. Regarding the resource extraction, it is related to a parameter that indicates the quality of the remaining mineral and fossil resources. In both cases, the extraction of these resources will result in higher energy requirements for future extraction.

The *cumulative energy demand* (CED) calculates the primary energy demand (Jungbluth and Frischknecht 2004), which is expressed as megajoule equivalents. The *method of ecological scarcity* (UBP'97) takes into account a comparative weighting and aggregation of various environmental interventions by use of so-called eco-factors, which are calculated from the present pollution level (current

Table 1 Case scenarios considered in this work

	Best scenario		Worst scenario	
	Distillation	Incineration	Distillation	Incineration
Ancillaries	–	–	–	–
Steam	From waste-solvent incineration	–	Average European production	–
Avoided steam production	–	Average European production[a] (100 % efficiency)	–	From natural gas[b] (90 % efficiency)
Electricity	CH	–	UCTE	–
Air treatment	Air incineration	–	VOCs	–
Residue 1	Distillation step 2	–	Distillation step 2	–
Residue 2	Incineration	–	Incineration	–

Recovery of solvents is 99 % for all the mixtures

[a] Steam (average production) from average European steam production using 76 % natural gas and 24 % heavy fuel oil

[b] Steam (from natural gas) using 100 % natural gas

flows) and on the pollution considered as critical (critical flows). The score is expressed as UBP. The *global warming potential* is calculated according to IPCC guidelines (IPPC 2001), and it is expressed as CO_2 equivalents. Finally, the *total CO_2* indicates the total CO_2 emissions of a complete CO_2 balance.

2.4 Case scenarios

In order to facilitate the decision-making processes in industry, two case scenarios have been considered. Distillation (batch and continuous) and incineration have been applied for the material or energy recovery of the waste solvent for

Table 2 Sustainability indicators for the mixture acetonitrile (A)–toluene (B)

Case	Target compound	Indicator	Mixture composition (wt% of acetonitrile)					
			25		50		75	
			Ba[a]	Co[b]	Ba[a]	Co[b]	Ba[a]	Co[b]
Best scenario	A	Eco-I 99			*D*	*D*	*D*	*D*
		UBP-97			*D*	*D*	*D*	*D*
		GWP	*I*	*I*				
		CED			*D*	*D*	*D*	*D*
		CO2						
Worst scenario	A	Eco-I 99					*D*	*D*
		UBP-97						*D*
		GWP	*I*	*I*				
		CED					*D*	*D*
		CO2	*I*	*I*			*D*	*D*
Best scenario	B	Eco-I 99						
		UBP-97						
		GWP						
		CED						
		CO2						
Worst scenario	B	Eco-I 99						
		UBP-97						
		GWP	*D*					
		CED						
		CO2	*D*	*D*				

The recovery is 99 % for the target compound

D distillation shows lower impact, *I* incineration shows lower impact

[a] Batch distillation

[b] Continuous distillation

each case scenario (Table 1). The best-case scenario tries to minimize the environmental burdens (and maximize the environmental credits), and the worst-case scenario assumes maximal environmental burdens (and minimal environmental credits; Capello et al. 2008). There is a large variation of the environmental impacts of 1 kWh of electricity depending on the technology used for electricity production (Itten et al. 2012). Today's electricity production in the European Union is dominated by nuclear power (29 %), natural gas (22 %), hard coal (20 %), lignite (11 %) and hydroelectric

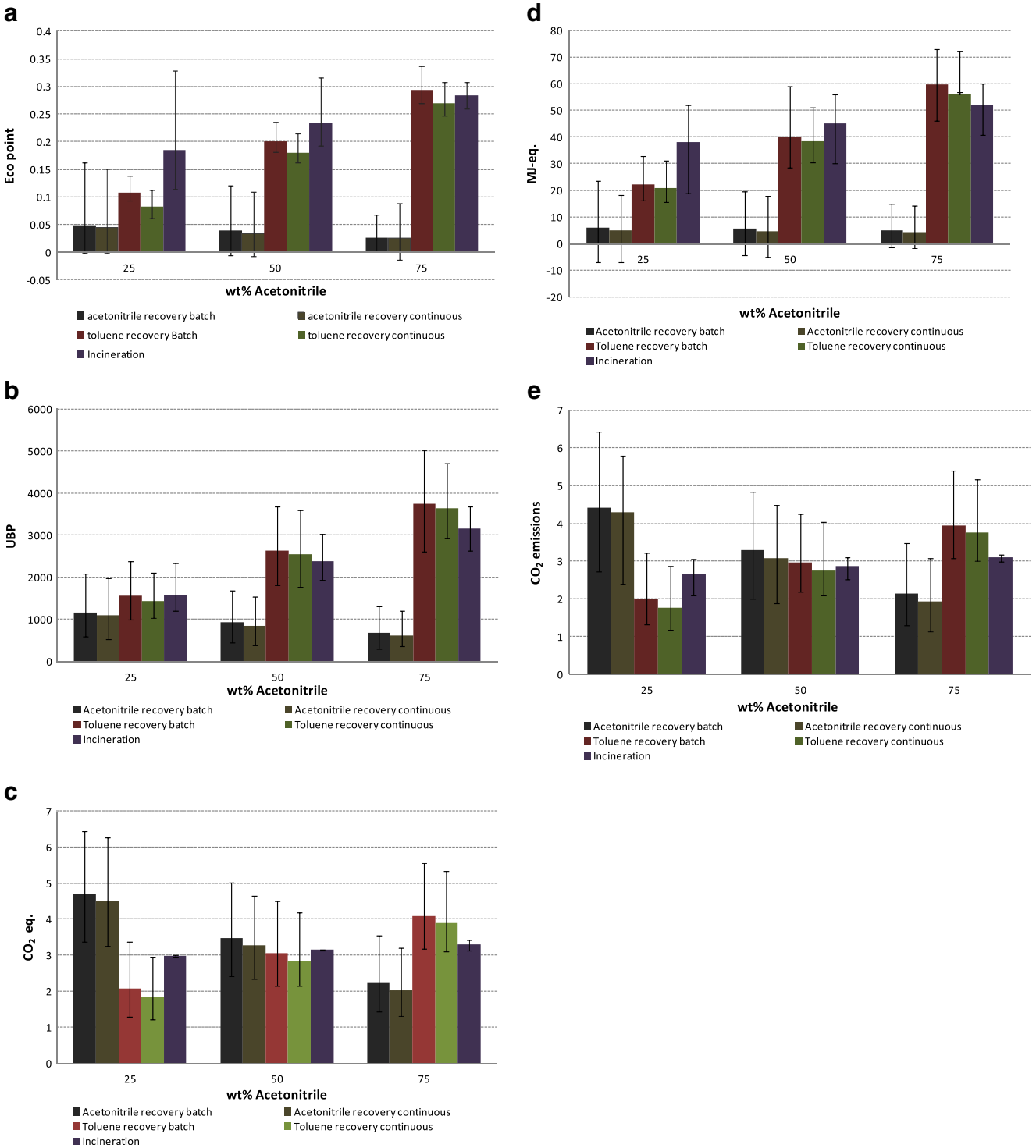

Fig. 1 Comparison of: **a** Eco-indicator 99, **b** UBP-97, **c** GWP, **d** CED and **e** total CO2 of the mixure acetonitrile–toluene for incineration and batch and continuous distillation with acetonitrile or toluene as target compounds (best case scenario)

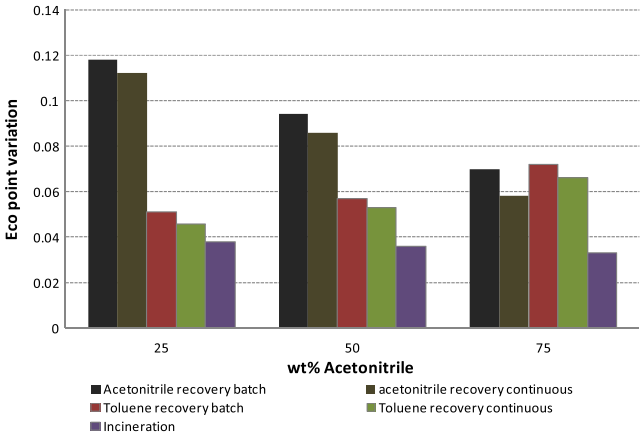

Fig. 2 Comparison between the best and worst scenarios for batch and continuous distillation and incineration

power (11 %). With a production share of 5 %, renewable energies other than hydroelectric power play so far only a minor role (Frischknecht and Stucki 2010). The European electricity mix causes greenhouse gas emissions equal to 462 g CO_2 eq/kWh, a cumulative energy demand of 10.3 MJ oil eq/kWh and a total environmental impact of 439 eco-points/kWh. In contrast, in Switzerland the electricity is mainly produced from hydropower (55.5 %) followed by nuclear power (44.5 %) and wastes (Itten et al. 2012). In this work, the Swiss electricity mix is considered the best scenario following the considerations taken by Capello et al. (2008) since it is practically free of CO_2 as well as other health and environment endangering emissions in spite of other issues concerning the management of nuclear waste, the damages produced if an accident occurs or the social

Table 3 Sustainability indicators for the mixture acetonitrile (A)–toluene (B)–THF (C)

Case	Target compound	Indicator	Mixture composition (wt% acetonitrile/toluene/THF)							
			33/33/33		50/25/25		25/50/25		25/25/50	
			Ba[a]	Co[b]	Ba[a]	Co[b]	Ba[a]	Co[b]	Ba[a]	Co[b]
Best scenario	A	Eco-I 99								
		UBP-97								
		GWP								
		CED								
		CO2					*I*			
Worst scenario	A	Eco-I 99								
		UBP-97								
		GWP								
		CED								
		CO2								
Best scenario	B	Eco-I 99								
		UBP-97								
		GWP								
		CED								
		CO2								
Worst scenario	B	Eco-I 99								
		UBP-97								
		GWP								
		CED								
		CO2								
Best scenario	C	Eco-I 99	*D*	*D*	*D*	*D*			*D*	*D*
		UBP-97							*D*	*D*
		GWP							*D*	*D*
		CED	*D*	*D*	*D*	*D*	*D*	*D*	*D*	*D*
		CO2							*D*	*D*
Worst scenario	C	Eco-I 99							*D*	*D*
		UBP-97								
		GWP							*D*	*D*
		CED							*D*	*D*
		CO2							*D*	*D*

The recovery is 99 % for the target compound

D distillation shows lower impact, *I* incineration shows lower impact

[a]Batch distillation

[b]Continuous distillation

acceptance. Thus, the best scenario for distillation considers the use the Swiss electricity mix (CH) as the source of electricity, and the worst scenario considers the average European electricity mix (UCTE) for electricity production. The residue from the first distillation step (residue 1) is sent to the second distillation step, and the residue produced in this second step (residue 2) is treated in a special waste-solvent incinerator, in both scenarios. In addition, the

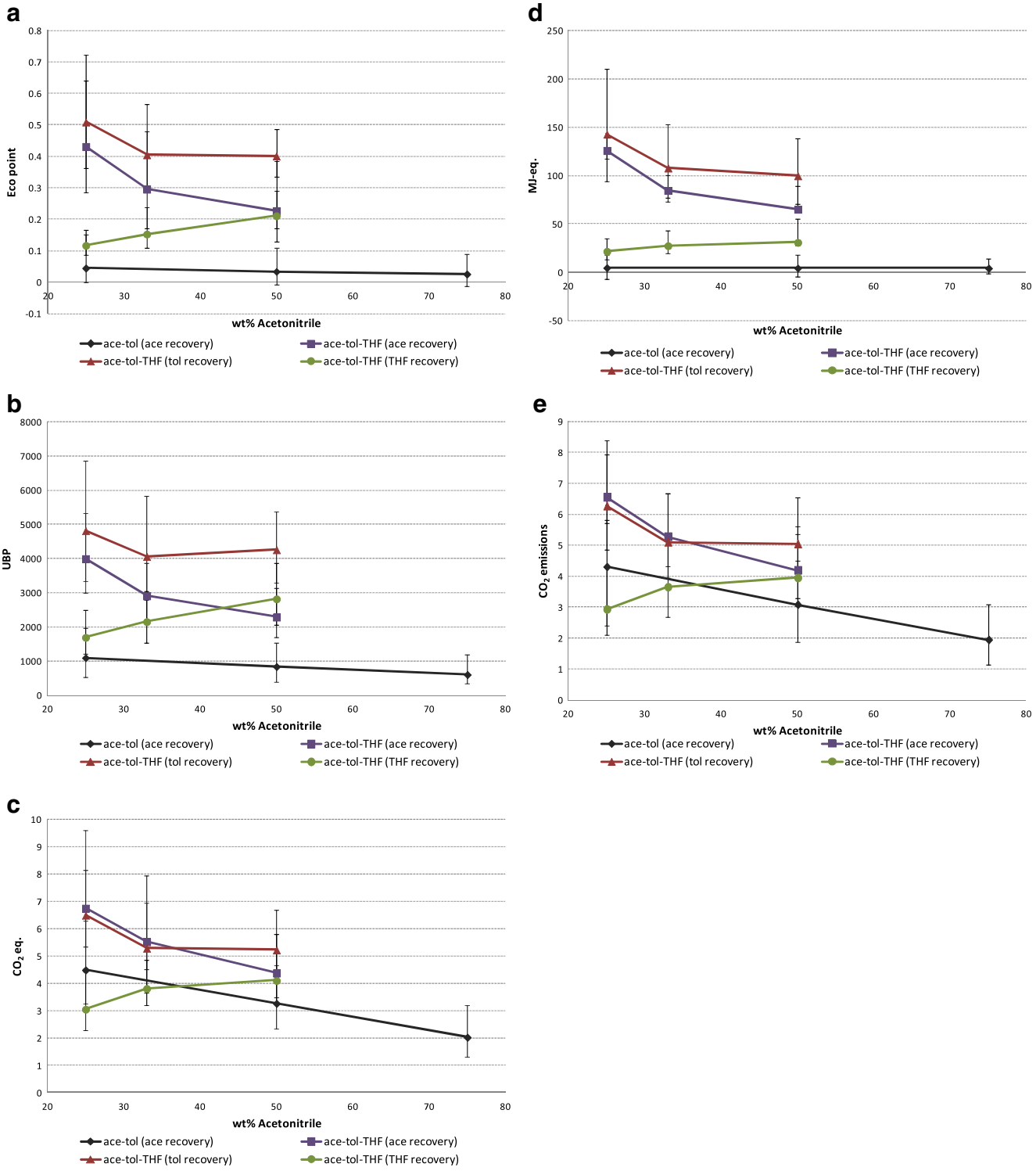

Fig. 3 Indicators for a mixture acetonitrile ('ace')–toluene ('tol') as a function of acetonitrile concentration with and without THF in the mixture: **a** Eco-indicator 99, **b** UBP-97, **c** GWP, **d** CED and **e** total CO2. The concentration with 25 wt% acetonitrile includes 50 wt% THF. The target compound is shown *in between brackets* and the recovery is performed by means of continuous distillation

Ecosolvent tool allows choosing the origin of the steam to be used in distillation. It may come from average production, natural gas or waste solvent incineration. In this study, the best scenario considers the steam from waste solvent incineration since it avoids the consumption of fossil fuels and produces less environmental burdens. On the other hand, the average European production in boiler house considers mixtures of natural gas and other fuels, and its use can be assumed to be the worst scenario. Outlet air incineration and outlet air emission (with production of volatile organic compounds, VOCs) are considered for the best and worst scenarios, respectively.

Regarding incineration, steam can be produced, and this production can be considered as a reduction of steam from other sources. In the best case, the production of steam from the worst source and maximum efficiency is avoided (i.e. the average European steam production, 76 % natural gas, 24 % heavy fuel oil with a theoretical efficiency of 100 %), whereas in the worst case, the production of steam from the best source and lower efficiency is avoided (i.e. natural gas with 90 % efficiency).

The amount of waste solvent used in the calculations as reference is 1 kg. Assuming linearity between product and consumption or emission is common is LCA, but it is only valid as long as emissions are below the legal emission limits since abatement techniques in the flue gas would be applied so that linearity applies no longer (Seyler et al. 2005).

2.5 Uncertainty of results

In order to determine the uncertainty of results, the Ecosolvent tool makes calculations by taking the parameter uncertainty of input and model parameters into account using stochastic modeling (Monte Carlo analysis) to quantify the uncertainty (Weber and Capello 2006). Therefore, the results are presented under uncertainty and not as exact values. Note that only uncertainty arising from the life cycle inventory analysis is quantified, whereas uncertainty of impact assessment factors cannot be considered. The span between the minimum and maximum value represents the 95 % interval. Figure S1 in the Electronic supplementary material (ESM) is included to help with the interpretation of the results. Results larger than 0 represent environmental burdens (e.g. due to the use of steam in the distillation process), and results below 0 denote environmental credits due to the avoidance of virgin solvent production (credits for solvent recovery) or fossil fuels (credits for the energy use of the waste solvent). For more information about the statistics of the method, we address readers to the manuscript by Capello et al. (2005).

3 Results and discussion

The results for the four studied mixtures are presented below. Regarding the sustainability indicators, values greater than 0 represent environmental burdens (e.g. use of steam in distillation), and results lower than 0 represent environmental credits due to the avoidance of virgin solvent production (credits for solvent recovery) or fossil fuels (credits for the energy use of the waste solvent; Weber and Capello 2006).

3.1 Mixture acetonitrile–toluene and acetonitrile–toluene–THF

The sustainability indicators for the mixture acetonitrile–toluene are shown in Table 2 for mixtures containing 25, 50 and 75 wt% of acetonitrile and considering batch and continuous distillation as alternative to incineration. The

Table 4 Sustainability indicators for the mixture ethyl acetate (A)–water

Case	Target compound	Indicator	Mixture composition (wt% of ethyl acetate)					
			25		50		75	
			Ba[a]	Co[b]	Ba[a]	Co[b]	Ba[a]	Co[b]
Best scenario	A	Eco-I 99			*D*	*D*	*D*	*D*
		UBP-97				*D*	*D*	*D*
		GWP					*D*	*D*
		CED				*D*	*D*	*D*
		CO2						*D*
Worst scenario	A	Eco-I 99					*D*	*D*
		UBP-97						*D*
		GWP						
		CED					*D*	*D*
		CO2					*D*	*D*

The recovery is 99 % for the target compound

D distillation shows lower impact

[a]Batch distillation

[b]Continuous distillation

dark grey indicates the cases in which the mean value of the indicator for distillation is lower than the overall range of the incineration, but the confidence interval can be partially overlapped, while the letter D highlights the cases where distillation is clearly better than incineration from a statistical point of view. The light grey and letter I have the same meaning for the incineration process. The empty spaces indicate no statistical difference between distillation and

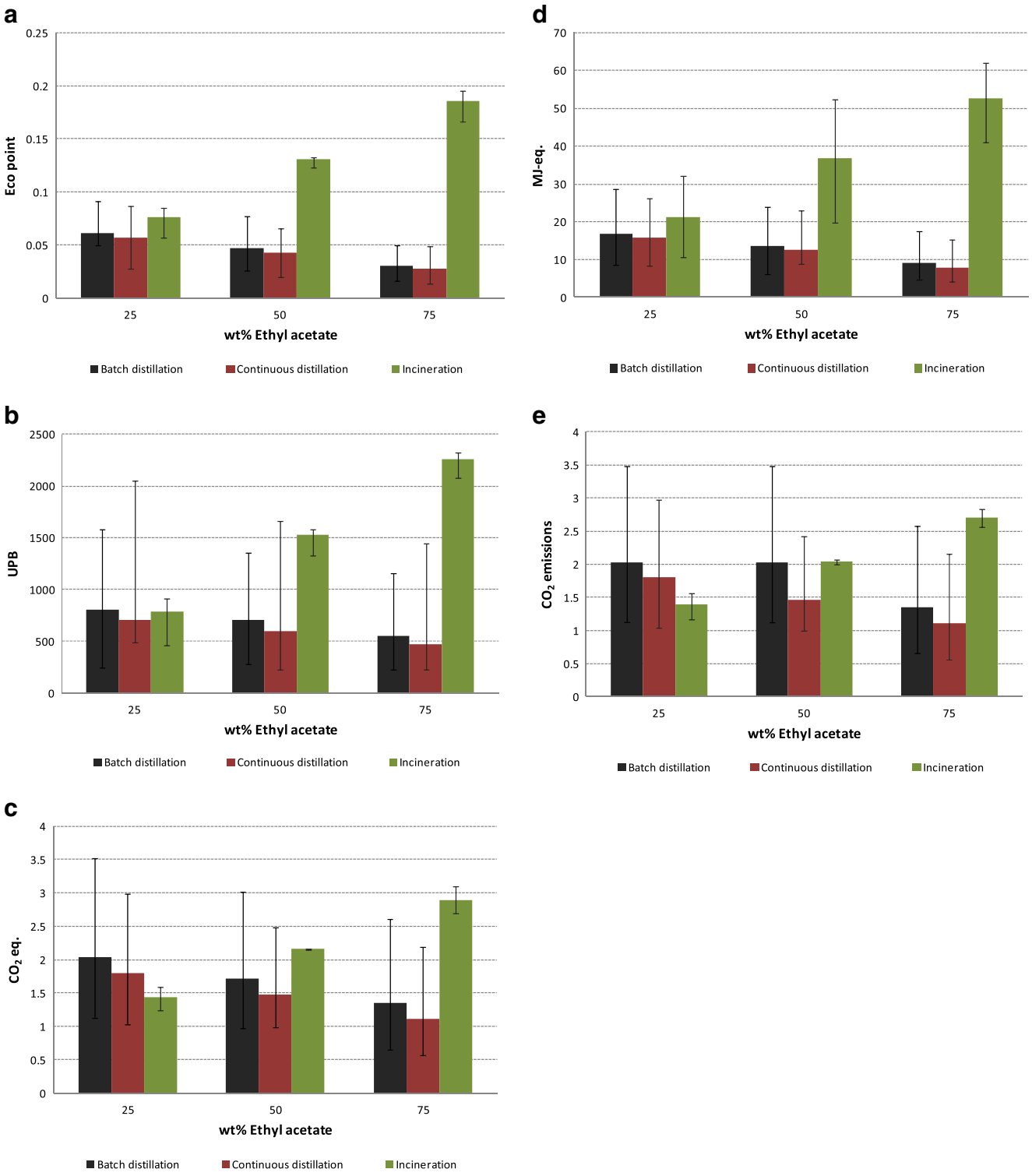

Fig. 4 Comparison of: **a** Eco-indicator 99, **b** UBP-97, **c** GWP, **d** CED and **e** total CO2 of the mixture ethyl acetate–water for incineration and batch and continuous distillation with ethyl acetate as target compound (best case scenario)

incineration from the environmental point of view. In a first glance, it can be observed in Table 2 that focusing the recovery on acetonitrile gives advantage to distillation, achieving a lower impact, and high concentrations of acetonitrile enhance the use of distillation. It is also worth noticing the differences obtained with some indicators, mainly those related directly with the energy consumption and CO_2 emissions. Since distillation is energetically a very intensive technology, low concentrations of acetonitrile (higher concentration of toluene) involve high energy requirements in distillation, leading to more environmental benefits when incineration is used. Recovery of toluene does not show preference for any of both technologies apart from mixtures highly concentrated in toluene, where distillation takes advantage.

Figure S2 in the ESM shows an example of the results for the Eco-indicator 99 for two different concentrations. It can be observed that the highest impact is caused by the solvent production. Thus, the recovery of the solvent with the highest environmental impact will play an important role in the reduction of the total impact. As evidenced in Fig. S2, the impact caused during the solvent production remains constant when the mixture composition is changed, but the recovery of acetonitrile decreases much more the total impact. Indeed, when high concentration of acetronitrile is in the mixture, distillation shows a clear advantage since the recovery of acetonitrile reduces significantly the total impact. However, higher concentration of toluene does not give such a significant advantage, and incineration is also competitive in terms of energy production. Thus, the composition of the mixture is a key issue in the decision making in order to select the waste-solvent treatment. The effect of the concentration on the Eco-indicator 99 can be also observed in Fig. 1a for continuous and batch distillation and incineration, and considering acetonitrile or toluene as the target compound. At high concentration of acetonitrile, the recovery of this compound seems to be the priority option from an environmental point of view. However, recovery of toluene by means of distillation shows an impact similar to incineration. At low concentration of acetonitrile, the confidence of the results is too low to establish conclusions about which compound should be the target one, although the average values indicate a preference for the recovery of acetonitrile and distillation shows advantage over incineration. Regarding batch or continuous distillation, there are no significant differences. The indicator UBP-97 and CED (Fig. 2b and d, respectively) show a similar trend with the difference that the UBPs caused by incineration are the same as those produced by distillation at low concentration of acetonitrile. Figure 2c, e shows the results for the indicator GWP (measured in CO_2 equivalents) and total CO_2 emissions, respectively. Both indicators follow a similar trend between each other but different to the other indicators. It is

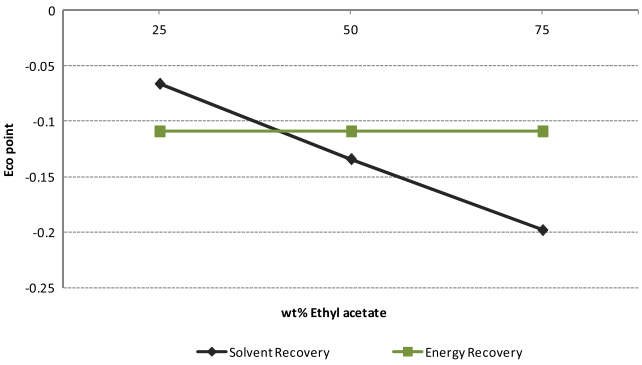

Fig. 5 Effect of solvent and energy recovery on Eco-Indicator 99 as a function of ethyl acetate concentration

interesting to highlight that recovery of acetonitrile at low concentration by means of distillation produces the highest emissions due to the demand of energy. Thus, toluene should be recovered. On the other hand, at high concentration of acetonitrile, the highest emissions are produced if toluene is the target compound to be recovered. Thus, considering all the indicators we can conclude that distillation (batch or continuous) is the most appropriate technology only when the most concentrated compound in the mixture is recovered. For 50 wt% acetonitrile mixtures, recovery of acetonitrile shows advantage according to the Eco-indicator 99, UBP-97 and CED, but regarding GWP and total emissions, there is no significant difference among technologies.

Figure 2 shows the comparison between the best and worst scenarios to check the variation of the Eco-indicator 99 depending on the initial considerations. The Eco point variation has been calculated as the value of the indicator in the worst scenario minus the value for the best scenario. It can be observed that the highest variations are obtained when acetonitrile is the target compound and decreases when its concentration increases. However, incineration shows a defined variation that does not depend on the composition of the mixture and presents the lowest value.

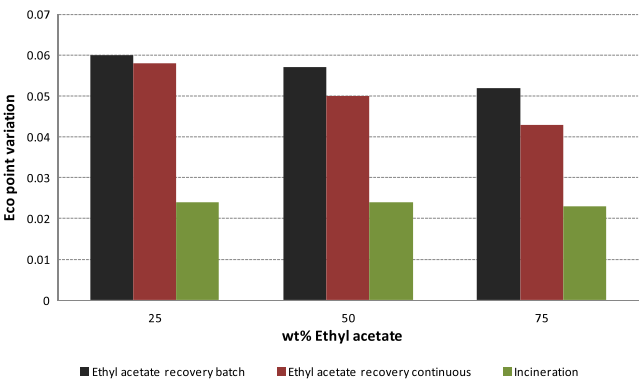

Fig. 6 Comparison between the best and worst scenarios for batch and continuous distillation and incineration with ethyl acetate as the compound to be recovered

This may be related with the uncertainty associated to the different technologies and the amount of the target solvent since the lower the concentration, the higher the variation. For toluene, some variation is also observed but not as significant as that for acetonitrile.

When acetonitrile is the target compound in a mixture of toluene containing THF (Table 3), distillation takes advantage if acetonitrile is the major compound. On the other hand, incineration seems to be better for some indicators (e.g. CO_2 balance) when toluene is present in higher concentration. Recovery of toluene does not show significant advantages for any technology, but when THF is the target compound, a clear priority for distillation can be established for all the range of waste-solvent concentrations. This can be also observed in Fig. S3 in the ESM, where the Eco-indicator 99 is shown for a mixture composed of 33 wt% of each component. Fig. S3a, S3b and S3c (ESM) refer to the cases where acetonitrile, toluene and THF are the target compounds, respectively. It can be observed that recovery of acetonitrile or toluene is not supported by statistical significance since the values of the ecoindicator are quite similar to those achieved by the use of incineration. However, when THF is aimed at its recovery the total impact decreases notably when distillation is used. In addition to this, Fig. S4 (ESM) shows that even when THF is in lower concentration in the mixture, its recovery is still the key factor that decreases significantly the total impact. Thus, it can be concluded that the solvent to be recovered should be the one that produces the highest impact during its manufacture, even if it is in lower quantity in the mixture, in order to minimize such impact. Thus, the recovery of THF by means of distillation is critical from an environmental point of view.

As a final comparison, Fig. 3 indicates the values of the studied indicators for different concentrations of acetonitrile in the mixture, with and without THF. The presence of THF tends to increase the total impact according to all the indicators, although special attention should be given to the indicators related to CO_2 emissions (i.e. GWP and total CO_2) since recovery of THF at low concentration of acetonitrile produces even lower emissions than those originated with mixtures acetonitrile–toluene (without THF). Thus, THF recovery is essential in order to minimize the impact. The recovery of the other compounds also produces a decrease of the total impact but much less significant.

3.2 Mixture ethyl acetate–water

Recovery of ethyl acetate by means of distillation is compared with incineration in Table 4. Batch or continuous distillation takes advantage at concentration of ethyl acetate higher than 50 wt%. However, it is also observed that when

Table 5 Sustainability indicators for the mixture methanol (A)–tetrahydrofurane (B)

Case	Target compound	Indicator	Mixture composition (wt% of methanol)					
			25		50		75	
			Ba[a]	Co[b]	Ba[a]	Co[b]	Ba[a]	Co[b]
Best scenario	A	Eco-I 99						
		UBP-97						
		GWP						
		CED						
		CO2						
Worst scenario	A	Eco-I 99						
		UBP-97						
		GWP						
		CED						
		CO2						
Best scenario	B	Eco-I 99	*D*	*D*	*D*	*D*	*D*	*D*
		UBP-97	*D*	*D*	*D*	*D*		*D*
		GWP	*D*	*D*	*D*	*D*		
		CED	*D*	*D*	*D*	*D*	*D*	*D*
		CO2	*D*	*D*	*D*	*D*		
Worst scenario	B	Eco-I 99	*D*	*D*	*D*	*D*		
		UBP-97	*D*	*D*	*D*	*D*		
		GWP	*D*	*D*	*D*	*D*		
		CED	*D*	*D*	*D*	*D*		
		CO2	*D*	*D*	*D*	*D*		

The recovery is 99 % for the target compound

D distillation shows lower impact

[a]Batch distillation

[b]Continuous distillation

the worst scenario is considered, the uncertainty of the results increases and distillation is statistically better than incineration for higher concentration of ethyl acetate in the mixture. For low concentration of ethyl acetate, both technologies show a similar impact. The main reason of this behaviour can be inferred from Fig. S5 in the ESM which shows the Eco-Indicator 99 for low (Fig. S5a, ESM) and high (Fig. S5b) concentration of ethyl acetate. The higher the concentration, the higher the impact originated by the production of the solvent and the higher is the reduction of that impact due to the solvent recovery. Thus, only when the amount of ethyl acetate recovered is high enough does the solvent recovery shows advantages with respect to the energy production from incineration. In addition, the total

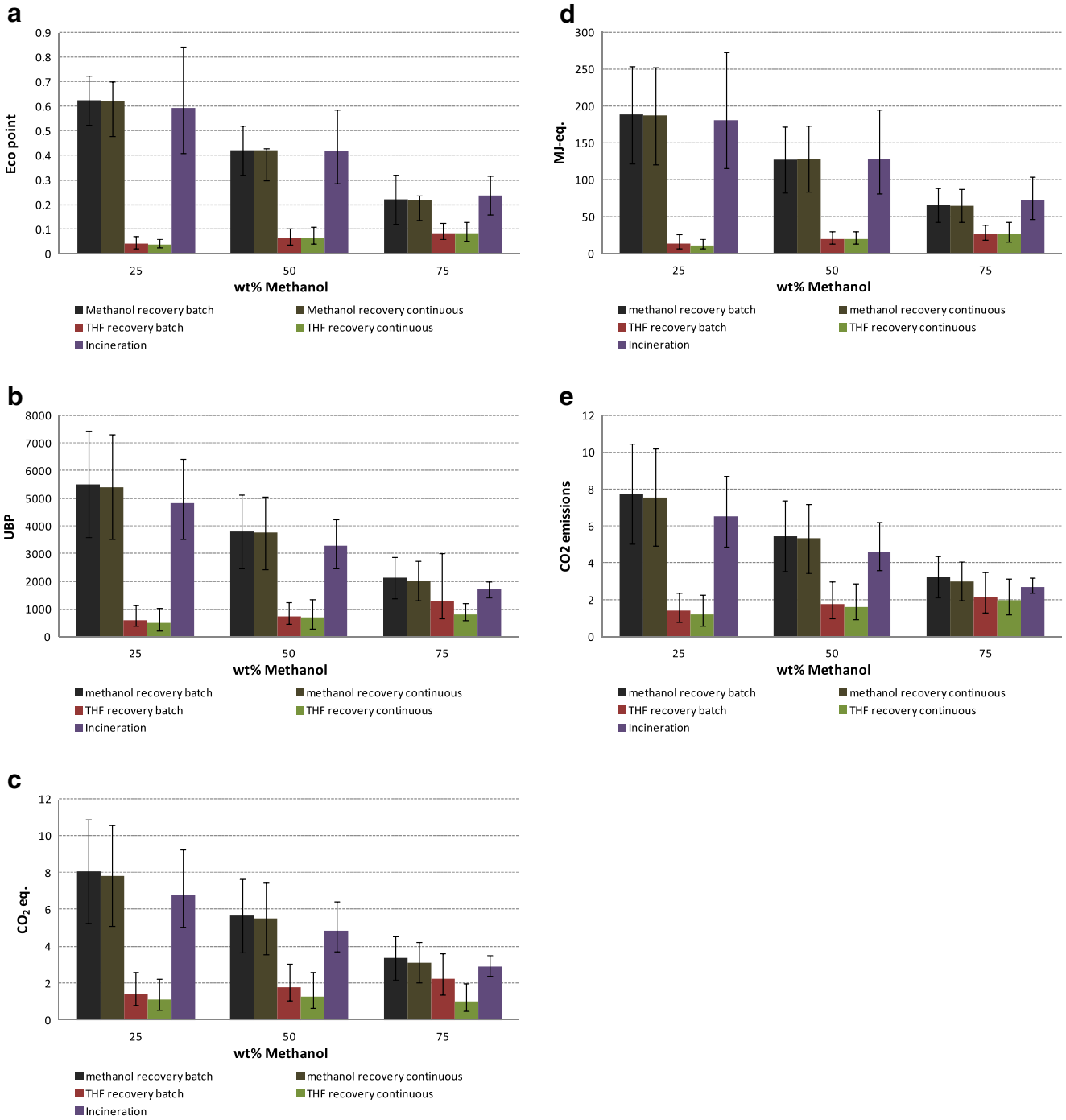

Fig. 7 Comparison of: **a** Eco-indicator 99, **b** UBP-97, **c** GWP, **d** CED and **e** total CO2 of the mixture methanol–THF for incineration and batch and continuous distillation with methanol or THF as target compounds to be recovered (best case scenario)

impact caused by the production and treatment of this organic–water mixture is lower than that produced from organic–organic mixtures, such as acetonitrile–toluene, due to the presence of water: the larger the concentration of ethyl acetate, the larger the impact. Higher environmental credits are obtained from the solvent recovery or energy production when more ethyl acetate is present, though.

The values for the Eco-Indicator 99, UBP-97, GWP, CED and total CO_2 for both kinds of distillation (batch and continuous) and incineration are shown in Fig. 4. The overall impact produced when distillation is used decreases when the concentration of ethyl acetate increases due to the solvent recovery. This trend is observed with all the indicators. On the contrary, higher concentration of ethyl acetate increases the impact given by all the indicators when incineration is used as the treatment technology. This occurs because the positive effect caused by the energy production does not depend on the concentration of ethyl acetate, as can be seen in Fig. 5 for the Eco-indicator 99. However, the decrease of the total impact caused by the ethyl acetate recovery varies linearly with the concentration; thus, the more solvent is recovered, the higher the impact minimization.

The differences between the best and worst scenarios for the Eco-indicator 99 can be observed in Fig. 6. This indicates the uncertainty to be assumed when not enough data are available during the design step. This uncertainty is higher for mixtures with low concentration of ethyl acetate, and it is smaller when incineration is considered.

3.3 Mixture methanol–tetrahydrofuran

A clear interest of distillation is observed (Table 5) in the treatment of mixtures methanol–THF when THF is the target compound. Recovery of methanol by means of distillation does not show a statistically significant decrease of the total impact. The study is then focused on the recovery of THF.

Figure S6 in the ESM shows the Eco-indicator 99 for high (Fig. S6a) and low (Fig. S6b) concentration of THF in the mixture. THF causes a large impact during its production, reaching around 0.75 Ecopoints (per kilogram of mixture) when there is 75 wt% of THF in the waste solvent, which is the highest value of the studied mixtures. Thus, it is expected that the recovery of THF produces a very significant decrease of the total impact. Indeed, Fig. S6a confirms that distillation is a better option than incineration, reducing the total impact below 0.2 Ecopoints. In addition, the energy production caused by incineration does not decrease the impact as much as solvent recovery, although its contribution to the total decrease is larger when more methanol is in the mixture (Fig. S6b, ESM). In addition, when waste solvents with lower concentrations of THF are treated by means of distillation, a lower impact caused by the solvent production is originated. Thus, the contribution of the impact decrease obtained with distillation is also lower.

Figure 7 shows that methanol recovery is not advantageous from an environmental point of view even at high concentration. Both technologies, distillation and incineration, produce a similar total impact for all the indicators. However, the recovery of THF is clearly necessary to decrease the high impact caused during the solvent production even if it is in a low concentration in the mixture. Only the indicator concerning the total CO_2 emissions shows no significant difference between distillation and incineration at low concentration of THF in the mixture.

4 Conclusions

The application of life cycle assessment as a tool during the decision making to determine which technology is the most appropriate for the treatment of waste solvents from an environmental point of view results in decisive conclusions in favour of distillation or incineration depending on the waste composition. In this work, it was observed that the main impact is caused during the solvent production. This means that those compounds of which the production entails a large environmental burden, such as tetrahydrofuran, should be recovered by means of distillation since the environmental credits obtained by the recovery are higher than those led by the energy production from incineration.

In general terms, when the impact caused during the solvent production is similar for the compounds in the mixture (e.g. acetonitrile–toluene), the recovery by means of distillation shows significant advantage when the target compound is highly concentrated in the mixture. In addition, organic–water mixtures are expected to produce lower environmental impact than organic–organic mixtures due to the significant impact caused during solvent production. Regarding batch and continuous distillation, no differences with statistical significance were observed.

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